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**WO 02/07883 A2**

(54) Title: **PRODUCTION OF HYDROCARBONS FROM A SYNTHESIS GAS**

(57) Abstract: A method of treating an untreated catalyst support includes contacting an untreated catalyst support which is partially soluble in an aqueous acid and/or a neutral aqueous solution with a modifying component precursor of the formula Me(OR)<sub>x</sub> where Me is a modifying component selected from Si, Zr, Ti, Cu, Zn, Mn, Ba, Co, Ni, Na, K, Ca, Sn, Cr, Fe, Li, Tl, Mg, Sr, Ga, Sb, V, Hf, Th, Ce, Ge, U, Nb, Ta, and W, R is an alkyl or acyl group, and x is an integer having a value of from 1 to 5. The modifying component is thereby introduced onto and/or into the catalyst support to form a protected modified catalyst support which is less soluble in the aqueous acid and/or the neutral aqueous solution. No calcination of the protected modified catalyst support is effected.

PRODUCTION OF HYDROCARBONS FROM A SYNTHESIS GAS

THIS INVENTION relates to the production of hydrocarbons from a synthesis gas, and to catalysts therefor. It relates in particular to a method of treating an untreated catalyst support to form a protected modified catalyst support, to a protected modified catalyst support thus formed, to a method of forming a catalyst from the protected modified catalyst support, to a catalyst thus obtained, to a process for producing hydrocarbons, and to hydrocarbons thus produced.

According to a first aspect of the invention, there is provided a method of treating an untreated catalyst support, which method includes contacting an untreated catalyst support which is partially soluble in an aqueous acid solution and/or in a neutral aqueous solution with a modifying component precursor of the formula  $\text{Me(OR)}_x$  where Me is a modifying component selected from Si, Zr, Ti, Cu, Zn, Mn, Ba, Co, Ni, Na, K, Ca, Sn, Cr, Fe, Li, Tl, Mg, Sr, Ga, Sb, V, Hf, Th, Ce, Ge, U, Nb, Ta, and W, R is an alkyl or acyl group, and x is an integer having a value of from 1 to 5, thereby to introduce the modifying component onto and/or into the catalyst support and to form a protected modified catalyst support which is less soluble or more inert in the aqueous acid solution and/or the neutral aqueous solution, than the untreated catalyst support, with no calcination of the catalyst support, after treatment thereof with the modifying component precursor, being effected.

The untreated catalyst support may, in particular, be in particulate form. The modifying component is thus present, in the protected modified catalyst support particles, on the particle surfaces, i.e. the modifying component is chemically bonded to the particle surfaces. The modifying component may be chemically bonded to OH (hydroxyl groups) on the support surfaces.

By 'calcination' is meant treatment of a catalyst support at an elevated temperature of at least 100°C to decompose organic groups of the modifying component in air, as well as to remove any residual solvent used for impregnation of the modifying component into or onto the catalyst support as hereinafter described. Thus, the present invention is characterized thereby that the protected modified catalyst support is not subjected to heat treatment at 100°C or higher. This naturally does not exclude possibly subjecting the protected modified catalyst support to heat treatment in excess of 100°C during subsequent transformation of the protected modified support into a catalyst precursor or into a catalyst, as hereinafter described.

The modifying component is thus capable, when present on the catalyst support, of suppressing the solubility of the untreated catalyst support in the aqueous acid solution and/or the neutral aqueous solution.

In principle, any commercially available dried, eg spray-dried, untreated catalyst support that is partially soluble in an aqueous acid solution and/or in a neutral aqueous solution, can be used. Examples of untreated catalyst supports that can be used are alumina ( $\text{Al}_2\text{O}_3$ ), titania ( $\text{TiO}_2$ ), magnesia ( $\text{MgO}$ ) and zinc oxide ( $\text{ZnO}$ ). When the catalyst support is alumina, any suitable alumina support can, in principle, be

used. For example, the alumina support may be that obtainable under the trademark Puralox SCCa 2/150 from SASOL Germany GmbH. Puralox SCCa 2/150 (trademark) is a spray-dried alumina support. Similarly, when the catalyst support is titania, any suitable titania support can, in principle, be used. For example, the titania support may be that obtainable under the trademark Degussa P25.

By 'untreated' in relation to the catalyst support is meant a catalyst support that is partially soluble in an aqueous acid solution and/or in a neutral aqueous solution.

The contacting of the untreated catalyst support with the modifying component precursor may be by means of impregnation or chemical vapour deposition; however, impregnation is preferred.

In one embodiment of the invention, the modifying component precursor may be a silicon-based modifying component precursor or an organic silicon compound, eg a silicon alkoxide, so that the modifying component is silicon (Si). The organic silicon compound may then be tetra ethoxy silane ('TEOS', i.e.  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) or tetra methoxy silane ('TMOS', i.e.  $\text{Si}(\text{OCH}_3)_4$ ).

When a silicon-based modifying component precursor is used with an alumina catalyst support, it may then be used in a quantity such that the silicon level in the resultant protected modified catalyst support is at least 0.06 Si atoms/nm<sup>2</sup> of the untreated support, preferably at least 0.13 Si atoms/nm<sup>2</sup> of the untreated support, and more preferably at least 0.26 Si atoms/nm<sup>2</sup> of the untreated support.

The upper limit of the modifying component, eg silicon, in the protected modified catalyst support may be set by parameters such as the

porosity of the protected modified catalyst support and/or by the average pore diameter of the protected modified catalyst support. Preferably, the average pore diameter of the protected modified catalyst support as hereinafter described is at least 12nm, as disclosed in ZA 96/2759, which is hence incorporated herein by reference thereto. Additionally, if an objective is to obtain, from the protected modified catalyst support, a catalyst having a composition of 30g Co/100g  $\text{Al}_2\text{O}_3$ , the untreated  $\text{Al}_2\text{O}_3$  catalyst support, and also the protected modified catalyst support, must have a pore volume of at least 0.43ml/g, as described in US 5733839, WO 99/42214 and/or WO 00/20116, which are thus incorporated herein by reference. The upper limit of the modifying component, e.g. Si, in the protected modified catalyst support is thus to be selected in such a manner that the geometry, e.g. the average pore diameter and porosity, of the protected modified catalyst support is not detrimentally effected to an appreciable extent.

Thus, when spray-dried Puralox SCCa 2/150 (trademark) alumina is used as the untreated catalyst support, sufficient silicon-based modifying component precursor is used such that the upper limit of silicon in the resultant protected modified catalyst support is 2.8 Si atoms/nm<sup>2</sup> of untreated catalyst support, preferably 2.5 Si atoms/nm<sup>2</sup> of untreated catalyst support, as taught in WO 99/42214.

The maximum amount of silicon that can be added to the untreated catalyst support in one impregnation step is 2.8 Si atoms/nm<sup>2</sup> of untreated catalyst support.

When the contacting of the catalyst support with the silicon-based modifying component precursor or organic silicon compound is effected by way of impregnation, the organic silicon compound will be dissolved

in an impregnation solvent having a boiling point, at atmospheric pressure, of less than 100°C. The impregnation solvent is typically an organic solvent capable of dissolving the silicon compound, such as ethanol, acetone or propanol. The untreated catalyst support may then  
5 be admixed with the resultant solution to form a treatment mixture, and the treatment mixture maintained at an elevated temperature for a period of time to impregnate the modifying agent into and/or onto the catalyst support. The elevated temperature may be at or near the boiling point of the impregnation solvent. The impregnation may be  
10 effected at atmospheric pressure, and the period of time for which the impregnation is effected may be from 1 minute to 20 hours, preferably from 1 minute to 5 hours. The excess solvent or solution is then removed, ie the impregnated support is dried, to obtain the protected modified catalyst support. The drying may be effected under a drying  
15 pressure or vacuum of 0.01 to 1 bar(a), more preferably 0.01 to 0.3 bar(a), and at a temperature equal to the boiling point of the solvent at the drying pressure, eg using known drier equipment, fitted with a mixing device, and of which the jacket temperature is thus higher than the solvent boiling point. However, the drying temperature will be  
20 lower than 100°C.

In another embodiment of the invention, the modifying component precursor may be a zirconium alkoxide, eg zirconium isopropoxide ( $\text{Zr}(\text{OCH}(\text{CH}_3)_2)_4$ ), so that the modifying component is zirconium (Zr). The  
25 contacting of the untreated catalyst support with the zirconium alkoxide may then be effected in similar fashion to the contacting hereinbefore described for the silicon-based modifying component precursor.

According to a second aspect of the invention, there is provided a  
30 method of treating an untreated catalyst support, which method includes

- admixing an untreated catalyst support which is partially soluble in an aqueous acid solution and/or in a neutral aqueous solution, with a solution of a modifying component precursor of the formula  $\text{Me(OR)}_x$  where Me is a modifying component selected from Si, Zr, Ti, Cu, Zn, Mn, Ba, Co, Ni, Na, K, Ca, Sn, Cr, Fe, Li, Tl, Mg, Sr, Ga, Sb, V, Hf, Th, Ce, Ge, U, Nb, Ta, and W, R is an alkyl or acyl group, and x is an integer having a value of from 1 to 5, in an impregnation solvent having a boiling point, at atmospheric pressure, of less than 100°C, to form a treatment mixture;
- 10 maintaining the treatment mixture at or near the boiling point of the impregnated solvent for from 1 minute to 20 hours, to impregnate the catalyst support with the modifying component; and
- drying the impregnated support by removing excess solvent or solution under a vacuum of 0.01 to 1 bar(a), thereby to obtain a
- 15 protected modified catalyst support which is less soluble or more inert in the aqueous acid solution and/or the neutral aqueous solution than the untreated catalyst support, with no calcination of the catalyst support, after treatment thereof with the modifying component precursor, being effected, and with the modifying component thus
- 20 being capable, when present in and/or on the protected modified catalyst support, of suppressing the solubility of the protected modified catalyst support in the aqueous solution.
- The method may include washing the protected modified catalyst
- 25 support to remove any residual solvent, with a slurry comprising the washed catalyst support and washing liquid being formed, and drying the slurry.
- The washing may be effected with an aqueous solution, and may be
- 30 effected at a temperature of about 60°C for a period of time, eg for about 1 hour.

The drying of the slurry may be effected at a temperature of about 95°C, and under a vacuum of between 0.03 bar(a) and 0.2 bar(a).

- 5 The invention extends to a protected modified catalyst support, when obtained by the method as hereinbefore described.

According to a third aspect of the invention, there is provided a method of forming a catalyst precursor, which method comprises mixing a  
10 protected modified catalyst support as hereinbefore described, with an aqueous solution of an active catalyst component or its precursor, to form a slurry, and impregnating the protected modified catalyst support with the active catalyst component or its precursor, to form the catalyst precursor.

15

The active catalyst component precursor may be cobalt nitrate so that the active catalyst component in and on the catalyst is cobalt. The untreated catalyst support may, as hereinbefore described, be alumina.

- 20 The method of forming the catalyst precursor may be in accordance with that described in US 5733839, WO 99/42214, and/or WO 00/20116, which are thus incorporated herein by reference. Thus, the mixing of the protected modified catalyst support and the active catalyst component or its precursor aqueous solution, and the  
25 impregnating, may comprise subjecting a slurry of the protected modified catalyst support or carrier, water and the active catalyst component or its precursor to a sub-atmospheric pressure environment, drying the resultant impregnated carrier under a sub-atmospheric pressure environment, and calcining the dried impregnated carrier, to  
30 obtain the catalyst precursor, ie to obtain a Fischer-Tropsch catalyst in unreduced form.



If a higher catalyst cobalt loading is required, then a second or even a third impregnation, drying and calcination step may thereafter be carried out after the first impregnation, drying and calcination step hereinbefore  
5 described.

During the impregnation, a water soluble precursor salt of platinum (Pt) or palladium (Pd) may be added, as a dopant capable of enhancing the reducibility of the active component. The mass proportion of this  
10 dopant, when used, to active catalyst component may be between 0.01:100 and 0.3:100.

The invention extends also to a catalyst precursor, when obtained by the method as hereinbefore described.

15

This catalyst precursor is thus in unreduced form, and requires reduction or activation before it can be used, ie it requires reduction or activation to be converted to a catalyst. This may be effected by subjecting the precursor to heat treatment under the influence of a  
20 reducing gas such as hydrogen, to obtain the catalyst.

Thus, according to a fourth aspect of the invention, there is provided a method of forming a catalyst, which includes reducing or activating a catalyst precursor as hereinbefore described.

25

The invention thus extends also to a catalyst, when obtained by the method as hereinbefore described.

According to a fifth aspect of the invention, there is provided a process  
30 for producing hydrocarbons, which includes contacting a synthesis gas comprising hydrogen and carbon monoxide at an elevated temperature

between 180°C and 250°C and an elevated pressure between 10 and 40 bar with a catalyst as hereinbefore described, to obtain hydrocarbons, by means of a slurry phase Fischer-Tropsch reaction of the hydrogen with the carbon monoxide.

5

The invention extends also to hydrocarbons, when produced by the process as hereinbefore described.

It is known that an alumina supported cobalt based slurry phase Fischer-Tropsch catalyst produces a wax product when used in a  
10 Fischer-Tropsch reaction of a synthesis gas, comprising hydrogen and carbon monoxide.

Such catalysts have hitherto preferably been produced by slurry  
15 impregnation of an alumina support using an aqueous cobalt nitrate precursor solution, of which the pH can vary between 1 and 6. The alumina support partially dissolves in aqueous acid, as well as neutral aqueous solutions. After dissolution, the aluminium ions can, in the presence of cobalt ions:

- 20 (i) re-precipitate as hydrotalcite-like structures, eg  $\text{Co}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ ; and/or  
(ii) re-precipitate as boehmite ( $\text{AlOOH}$ ).

These re-precipitated aluminium structures are postulated to be physically bonded and loosely adsorbed to the original alumina surface.  
25 The formation of irregular structures on the surfaces of supports present after impregnation of, respectively, alumina with an aqueous nickel nitrate solution, magnesia with an aqueous ruthenium chloride solution and titania with an aqueous platinum chloride solution is also found. This phenomenon is thus not limited to alumina ( $\text{Al}_2\text{O}_3$ ), but can  
30 also be found when using alternative supports such as magnesia ( $\text{MgO}$ ), titania ( $\text{TiO}_2$ ) or zinc oxide ( $\text{ZnO}$ ).

A serious problem that can arise when such catalysts, which are thus prepared on untreated catalyst supports, are used, as observed during larger scale pilot plant Fischer-Tropsch synthesis runs, is the undesired high cobalt content of the wax product. Testing of the slurry phase Fischer-Tropsch synthesis process, using the known untreated alumina supported cobalt catalyst, can result in the wax product containing more than 50 mass ppm cobalt, even after secondary ex-situ filtration through a Whatmans 42 (trademark) filter paper (hereinafter referred to as "secondary filtered wax product". During slurry impregnation of an untreated alumina support, using an aqueous cobalt nitrate solution, cobalt nitrate will also deposit on the loosely bonded re-precipitated aluminium structures. These cobalt on loosely bonded re-precipitated aluminium structures can dislodge during extended Fischer-Tropsch synthesis runs, possibly aggravated by the hydrothermal nature of a realistic synthesis environment, and contaminate the wax product (hydrocarbon product that is a liquid at the applied Fischer-Tropsch synthesis conditions and withdrawn as such from the reactor) with cobalt rich ultra fines of a sub-micron nature. These cobalt rich ultra fine particulates, of submicron nature, exit the reactor in the wax product. Due to the high cost of cobalt, this is a highly undesirable problem which has thus been solved, or at least alleviated, with this invention. Said alumina support should thus be protected during aqueous slurry impregnation by improving the inertness of the alumina surface, to prevent formation of cobalt ultra fines during Fischer-Tropsch synthesis. This is achieved in the present invention.

The invention will now be described in more detail with reference to the following non-limiting examples and with reference to the accompanying drawings.

In the drawings

FIGURE 1 shows dissolution profiles for an untreated alumina support, and a silicon modified alumina support according to the Example 1;

5        FIGURE 2 shows dissolution profiles for an untreated titania support, and a silicon modified titania support according to Example 2;

FIGURE 3 shows dissolution profiles for an untreated alumina support, and a zirconium modified alumina support according to Example 3;

10       FIGURE 4 shows dissolution profiles for an untreated alumina support, and a titanium modified alumina support according to Example 4; and

FIGURE 5 shows the cobalt contamination level of secondary filtered wax product as a function of Fischer-Tropsch slurry phase synthesis time on stream as observed on Pilot Plant scale. Supported cobalt Fischer-Tropsch synthesis catalysts were compared, as obtained from an untreated particulate alumina support known by the trademark Puralox SCCa 2/150 (Catalyst B) and from a silicon modified alumina support (Catalyst A) in accordance with the invention.

20

#### EXAMPLE 1

##### Modification of alumina support with silicon

A spray-dried Puralox SCCa 2/150 (trademark) alumina support, in the form of spherical particles, obtainable from SASOL Germany GmbH of  
25    Überseering 40, 22297, Hamburg, Germany, was used. The support was thus an untreated support. The surfaces of the support particles were modified with silicon. An impregnation method was used to achieve the modification. Thus, silicon, in the form of TEOS (tetraethoxy silane) as precursor, was added to ethanol at 60°C. Ethanol  
30    was thus used as the impregnation solvent. The particulate alumina support was added to this solution, which was then kept at 50°C-75°C

for 1 hour. Subsequently, the solvent was removed under vacuum at 0.03-0.2bar(a), with a jacket temperature of the drier equipment of 95°C. No calcination was employed after the drying. A protected silicon modified alumina support was thus obtained. The aimed for  
5 silicon content was 2.5 Si atoms/nm<sup>2</sup> untreated support.

## EXAMPLE 2

### Modification of titania support with silicon

An untreated or fresh particulate titanium dioxide (Degussa P25  
10 (trademark)) support was calcined at 650°C for 16 hours, spray dried and classified to 75-150 micron. The support had a rutile content of 80% and a surface area of 27m<sup>2</sup>/g.

This support was modified in the same fashion as described in Example  
15 1 by addition of TEOS and drying at 95°C, to obtain a protected silicon modified titania support. No calcination was employed after the drying. The aimed for silicon content was 4.5 Si atoms/nm<sup>2</sup> untreated resh support.

## EXAMPLE 3

### Modification of alumina support with zirconium

Zirconium, in the form of zirconium isopropoxide as precursor, was added under an inert atmosphere to isopropanol. Isopropanol was thus used as the impregnation solvent. A particulate alumina support (which  
25 was the same as that used in Example 1) was added to this solution, and the mixture stirred at 60°C for 1 hour. The solvent was then removed under a vacuum of 0.03-0.2bar(a) with a jacket temperature of the drier equipment at 95°C. No calcination was employed after the drying. A protected zirconium modified alumina support was thus  
30 obtained. The aimed for amount of modifying component was 0.1 Zr atoms per square nanometer untreated support.

#### EXAMPLE 4

##### Modification of alumina support with titanium

A particulate alumina support, the same support as used in Example 1,  
5 was modified in the same fashion as described in Example 1, using  
TEOT (tetra ethyl ortho titanate) as the precursor rather than TEOS,  
with drying at 95°C. No calcination was employed after the drying. A  
protected titanium modified alumina support was thus obtained. The  
aimed for titanium content was 2.5 Ti atoms/nm<sup>2</sup> untreated support.

10

#### EXAMPLE 5

##### Conductivity measurements

Alumina and titania dissolve in an aqueous medium at low pH. The  
dissolution of alumina or titania results in the formation of aluminium  
15 ions or titanium ions respectively. As more and more alumina or titania  
dissolves, the concentration of aluminium or titanium ions increases  
with time. The increase of aluminium or titanium ions with time was  
followed by monitoring the conductivity at a constant pH of 2. The pH  
was kept constant by automated addition of a 10% nitric acid solution.

20

In Figure 1, the cumulative mg Al dissolved per m<sup>2</sup> untreated support  
for an untreated alumina as well as for the protected silicon modified  
alumina of Example 1 was plotted against time. It can be seen that the  
untreated pure alumina dissolved faster than the protected silicon  
25 modified alumina.

In Figure 2, the dissolution profiles of untreated titania as well as of the  
protected silicon modified titania of Example 2 are plotted. This Figure  
indicates that modification of the untreated titania brought about an  
30 increase in resistance to dissolution.

In Figure 3, the dissolution profile of the untreated Puralox SCCa 2/150 (trademark) alumina support is plotted against the dissolution profile of the protected zirconium modified alumina support of Example 3. Figure 3 shows that the addition of zirconium to the untreated support improved the resistance of the untreated support to dissolution and aqueous/acid attack.

In Figure 4, the cumulative mg Al dissolved per m<sup>2</sup> untreated support for an unmodified alumina as well as for the protected titanium modified alumina of Example 4 was plotted against time. It can be seen that the untreated pure alumina dissolved faster than the protected titanium modified alumina.

#### EXAMPLE 6

##### 1. Catalyst preparation

##### Catalyst A

A supported cobalt catalyst precursor was prepared on a protected silicon modified alumina support as prepared in Example 1. In a first impregnation / drying / calcination step, a solution of 17.4kg of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 9.6g of (NH<sub>3</sub>)<sub>4</sub>Pt(NO<sub>3</sub>)<sub>2</sub>, and 11kg of distilled water was mixed with 20.0kg of a silicon modified alumina support, by adding the support to the solution. The slurry was added to a conical vacuum drier and continuously mixed. The temperature of this slurry was increased to 60°C after which a pressure of 20kPa(a) was applied. During the first 3 hours of the drying step which commenced with the application of the pressure of 20kPa(a), the temperature was increased slowly and reached 95°C after the 3 hours. After the 3 hours, the pressure was decreased to 3-15kPa(a), and a drying rate of 2.5m%/h at the point of incipient wetness was used. The impregnation and drying took 9 hours to complete, after which the impregnated and dried catalyst support was immediately and directly loaded into a fluidized bed calciner. The

temperature of the dried impregnated catalyst support was about 75°C at the time of loading into the calciner. The loading took about 1 to 2 minutes, and the temperature inside the calciner remained at its set point of about 75°C. The catalyst was heated from 75°C to 250°C, using a heating rate of 0.5°C/min and an air space velocity of 1.0 m<sup>3</sup>/kg Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O/h, and kept at 250°C for 6 hours. To obtain a catalyst with a cobalt loading of 30gCo/100gAl<sub>2</sub>O<sub>3</sub>, a second impregnation/drying/calcination step was performed. A solution of 9.4kg of Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, 15.7g of (NH<sub>3</sub>)<sub>4</sub>Pt(NO<sub>3</sub>)<sub>2</sub>, and 15.1kg of distilled water was mixed with 20.0kg of the ex first impregnated and calcined intermediate, by adding this material to the solution. The slurry was added to a conical vacuum drier and continuously mixed. The temperature of this slurry was increased to 60°C after which a pressure of 20kPa(a) was applied. During the first 3 hours of the drying step which commenced with the application of the pressure of 20kPa(a), the temperature was increased slowly and reached 95°C after the 3 hours. After the 3 hours, the pressure was decreased to 3-15kPa(a), and a drying rate of 2.5m%/h at the point of incipient wetness was used. The impregnation and drying took 9 hours to complete, after which the catalyst support was immediately and directly loaded into the fluidized bed calciner. The temperature of the dried impregnated intermediate material was about 75°C at the time of loading into the calciner. The loading took about 1 to 2 minutes, and the temperature inside the calciner remained at its set point of about 75°C. The impregnated and dried material was heated from 75°C to 250°C, using a heating rate of 0.5°C/min and an air space velocity of 1.0 m<sup>3</sup>/kg Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O/h, and kept at 250°C for 6 hours.



### Catalyst B

A supported cobalt catalyst precursor was prepared in a similar manner to that described hereinbefore for Catalyst A, except that the catalyst precursor was prepared on an untreated alumina support.

5

### 2. Pilot Plant slurry phase Fischer-Tropsch Synthesis Test

During a confidential Pilot Plant slurry phase Fischer-Tropsch synthesis test run, using 5kg of catalyst prepared on unmodified alumina, ie catalyst B, in a 11m high bubble column reactor with an external  
10 recycle, the secondary filtered wax product turned grey after about 10 days on stream and the cobalt content increased to 350ppm after 25 days on stream, as shown in Figure 5. The test runs were completed under realistic Fischer-Tropsch synthesis conditions:

15 Reactor temperature: 230 °C

Reactor pressure: 20 Bar

%(H<sub>2</sub> + CO) conversion: 50-70%

Feed gas composition:

H<sub>2</sub>: about ('ca') 50 vol%

20 CO: ca 25 vol%

Balance: Ar, N<sub>2</sub>, CH<sub>4</sub> and or CO<sub>2</sub>

The wax product produced in the Fischer-Tropsch synthesis test run was thus subjected to a primary solids separation step, and thereafter  
25 to secondary ex-situ filtration through Whatmans 42 (trademark) filter paper, to obtain the secondary filtered wax product.

The presence of a high cobalt content in the secondary filtered wax product is believed to be due to the dislodgment of cobalt crystallites  
30 that were deposited on top of the physically bonded re-precipitated aluminium structures (eg hydrotalcites, boehmite), present in the

catalyst after aqueous slurry phase impregnation of cobalt, when the catalyst is prepared from an untreated catalyst support.

Pilot Plant slurry phase Fischer-Tropsch synthesis tests runs performed  
5 on catalyst A, prepared on the modified alumina support with a silicon  
loading of 2.5 Si atoms/nm<sup>2</sup> untreated support, showed a substantial  
improvement with respect to the submicron cobalt particulate  
contamination in the secondary filtered wax product, as is evident from  
Figure 5. After 22 days on stream the catalyst with 2.5 Si atoms/nm<sup>2</sup>  
10 untreated support did not show any cobalt in these secondary filtered  
wax product.

From the Pilot Plant synthesis tests, it can be seen that the  
improvement of the inertness of the untreated alumina support by  
15 modifying it with silica, as shown by conductivity measurements, also  
prevented the dislodging of ultra fine cobalt rich particulates.

### 3. Laboratory Slurry Phase Fischer-Tropsch Synthesis

Cobalt catalyst precursors were reduced prior to Fischer-Tropsch  
20 synthesis in a tubular reactor at a hydrogen space velocity of 200ml,  
hydrogen/g catalyst/h and atmospheric pressure. The temperature was  
increased to 425 °C at 1°C/min, after which isothermal conditions were  
maintained for 16 hours.

25 Between 10g and 30g of the resultant reduced catalyst, ranging  
between 38 µm to 150 µm, was suspended in 300 ml molten wax and  
loaded in a CSTR with an internal volume of 500 ml. The feed gas  
consisted of hydrogen and carbon monoxide in a H<sub>2</sub>/CO molar ratio from  
1.5/l to 2.3/l. This reactor was electrically heated and sufficiently high  
30 stirrer speeds were employed so as to eliminate any gas-liquid mass  
transfer limitations. The feed flow was controlled by means of Brooks

mass flow controllers, and space velocities ranging from 2 and  $4\text{m}^3_n/\text{kg}_{\text{cat}}\text{hr}$  were used. GC analyses of the permanent gases as well as the volatile overhead hydrocarbons were used in order to characterize the product spectra.

5

The laboratory test runs were completed under realistic Fischer-Tropsch synthesis conditions:

Reactor temperature: 220°C

Reactor pressure: 20 bar

10 

%(H<sub>2</sub> + CO) conversion: 50-70%

Feed gas composition:

H<sub>2</sub>: ca 50 vol%

CO: ca 25 vol%

Balance: Ar, N<sub>2</sub>, CH<sub>4</sub> and/or CO<sub>2</sub>

15

Having applied a reported cobalt based Fischer-Tropsch kinetic equation, such as:

$$r_{\text{FT}} = (k_{\text{FT}} P_{\text{H}_2} P_{\text{CO}}) / (1 + K P_{\text{CO}})^2$$

20 the Arrhenius derived pre-exponential factor of  $k_{\text{FT}}$  was estimated for each of the reported runs. By defining the relative intrinsic Fischer-Tropsch activity as (pre-exponential factor of catalyst X after reduction test)/(pre-exponential factor of catalyst B), where X is catalyst A or B, the intrinsic Fischer-Tropsch activities of the cobalt catalysts could be  
25 compared. The initial relative intrinsic Fischer-Tropsch activity is determined after 15 hours on line, as given in Table 1. It is clear that support modification did not influence the intrinsic Fischer-Tropsch characteristics when compared to the untreated alumina supported cobalt catalyst, Catalyst B.

30

Table 1: Laboratory CSTR Fischer-Tropsch synthesis performance comparison between catalysts prepared on untreated (catalyst B) and silicon modified alumina supports (catalyst A).

	Catalyst A	Catalyst B
Run number	363F	233\$
<u>Synthesis conditions:</u>		
Calcined catalyst mass (g)	22.2	20.6
Reactor temp (°C)	220.0	221.0
Reactor pressure(bar)	20.0	20.0
Time on stream (h)	16.0	15.0
<u>Feed gas composition:</u>		
H <sub>2</sub> (vol%)	52.6	52.2
CO(vol%)	27.9	26.4
(Balance = Ar, CH <sub>4</sub> + CO <sub>2</sub> )		
Syngas (H <sub>2</sub> + CO) space velocity (m <sup>3</sup> <sub>n</sub> /(kg cat.h))	3.6	3.0
<u>Reactor partial pressures (bar)</u>		
H <sub>2</sub>	5.5	4.5
CO	2.9	2.5
H <sub>2</sub> O	4.5	4.8
CO <sub>2</sub>	0.3	0.3
<u>Synthesis performance</u>		
Conversion: %syngas	61.7	68.3
Initial relative intrinsic FT activity	1.0	1.0
%CO of total amount of CO converted to CO <sub>2</sub>	1.3	3.3
%C-atom CH <sub>4</sub> selectivity	5.3	4.3

5

The catalyst of the present invention, obtained by impregnating a protected modified catalyst support according to the invention, was found to have excellent Fischer-Tropsch synthesis behaviour, resulting

10

in high activity and selectivity. It was surprisingly found that the modified support material does not have to be calcined, after impregnation with the modifying component precursor and subsequent drying, to have the required inertness in aqueous media. These  
5 protected modified supports thus have an increased inertness towards an aqueous attack during subsequent slurry phase impregnation. Using catalysts prepared on these protected modified supports has resulted in a dramatic decrease in the formation of active phase-containing ultra-fine particulates during slurry phase Fischer-Tropsch synthesis. A slurry  
10 phase Fischer-Tropsch process, using the modified supported catalyst, produced a secondary filtered wax product containing less than 50ppm active phase ultra fines throughout extended slurry phase Fischer-Tropsch synthesis runs, thus reducing the cost for the catalyst used in the slurry phase Fischer-Tropsch process substantially. Due to the  
15 extreme difficulty with which separation of submicron particulates from wax product is achieved, the problem of removing solids from this wax product has thus been alleviated considerably.

CLAIMS

1. A method of treating an untreated catalyst support, which  
5 method includes contacting an untreated catalyst support which is partially soluble in an aqueous acid solution and/or in a neutral aqueous solution with a modifying component precursor of the formula  $\text{Me(OR)}_x$ , where Me is a modifying component selected from Si, Zr, Ti, Cu, Zn, Mn, Ba, Co, Ni, Na, K, Ca, Sn, Cr, Fe, Li, Tl, Mg, Sr, Ga, Sb, V, Hf, Th,  
10 Ce, Ge, U, Nb, Ta, and W, R is an alkyl or acyl group, and x is an integer having a value of from 1 to 5, thereby to introduce the modifying component onto and/or into the catalyst support and to form a protected modified catalyst support which is less soluble or more inert in the aqueous acid solution and/or the neutral aqueous solution, than  
15 the untreated catalyst support, with no calcination of the catalyst support, after treatment thereof with the modifying component precursor, being effected.
2. A method according to Claim 1, wherein the untreated  
20 catalyst support is in particulate form, with the modifying component being present, in the protected modified catalyst support particles, on the particle surfaces by being chemically bonded to the particle surfaces.
- 25 3. A method according to Claim 2, wherein the modifying component is chemically bonded to hydroxyl groups on the support particle surfaces.
4. A method according to any one of Claims 1 to 3 inclusive,  
30 wherein the contacting of the untreated catalyst support with the modifying component precursor is by means of impregnation.

5. A method according to Claim 4, wherein the modifying component precursor is an organic silicon compound, so that the modifying component is silicon.
- 5 6. A method according to Claim 5, wherein the organic silicon compound is tetra ethoxy silane or tetra methoxy silane.
7. A method according to Claim 5 or Claim 6, wherein the untreated catalyst support is an alumina catalyst support, with the  
10 silicon-based modifying component precursor being used in a quantity such that the silicon level in the resultant protected modified catalyst support is at least 0.06 Si atoms/nm<sup>2</sup> of the untreated catalyst support.
8. A method according to Claim 7, wherein the untreated  
15 alumina support is spray-dried Puralox SCCa 2/150 (trademark), with sufficient silicon-based modifying component precursor being used such that the upper limit of silicon in the resultant protected modified catalyst support is 2.8 Si atoms/nm<sup>2</sup> of untreated catalyst support.
- 20 9. A method according to any one of Claims 5 to 8 inclusive, wherein the organic silicon compound is dissolved in an impregnation solvent having a boiling point, at atmospheric pressure, of less than 100°C, with the catalyst support being admixed with the resultant solution to form a treatment mixture, and the treatment mixture  
25 maintained at an elevated temperature at or near the boiling point of the impregnation solvent for a period of time to impregnate the modifying agent into and/or onto the catalyst support.
10. A method according to Claim 9, wherein the impregnation  
30 is effected at atmospheric pressure, and the period of time for which the impregnation is effected is from 1 minute to 20 hours.

11. A method according to Claim 9 or Claim 10, wherein the impregnated support is dried to obtain the protected modified catalyst support, with the drying being effected under a drying pressure or vacuum of 0.01 to 1 bar(a), and at a temperature equal to the boiling point of the solvent at the drying pressure.

12. A method according to Claim 4, wherein the modifying component precursor is a zirconium alkoxide so that the modifying component is zirconium.

13. A method according to Claim 12, wherein the zirconium alkoxide is dissolved in an impregnation solvent having a boiling point, at atmospheric pressure, of less than 100°C, with the catalyst support being admixed with the resultant solution to form a treatment mixture, and the treatment mixture maintained at an elevated temperature at or near the boiling point of the impregnation solvent for a period of time to impregnate the modifying agent into and/or onto the catalyst support.

14. A method according to Claim 13, wherein the impregnation is effected at atmospheric pressure, and the period of time for which the impregnation is effected is from 1 minute to 20 hours.

15. A method according to Claim 13 or Claim 14, wherein the impregnated support is dried to obtain the protected modified catalyst support, with the drying being effected under a drying pressure or vacuum of 0.01 to 1 bar(a), and at a temperature equal to the boiling point of the solvent at the drying pressure.

16. A method of treating an untreated catalyst support, which method comprises



- admixing an untreated catalyst support which is partially soluble in an aqueous acid solution and/or in a neutral aqueous solution, with a solution of a modifying component precursor of the formula  $\text{Me(OR)}_x$  where Me is a modifying component selected from Si, Zr, Ti, Cu, Zn, Mn, Ba, Co, Ni, Na, K, Ca, Sn, Cr, Fe, Li, Tl, Mg, Sr, Ga, Sb, V, Hf, Th, Ce, Ge, U, Nb, Ta, and W, R is an alkyl or acyl group, and x is an integer having a value of from 1 to 5, in an impregnation solvent having a boiling point, at atmospheric pressure, of less than 100°C, to form a treatment mixture;
- 10 maintaining the treatment mixture at or near the boiling point of the impregnated solvent for from 1 minute to 20 hours, to impregnate the catalyst support with the modifying component; and
- drying the impregnated support by removing excess solvent or solution under a vacuum of 0.01 to 1 bar(a), thereby to obtain a
- 15 protected modified catalyst support which is less soluble or more inert in the aqueous acid solution and/or the neutral aqueous solution than the untreated catalyst support, with no calcination of the catalyst support, after treatment thereof with the modifying component precursor, being effected, and with the modifying component thus
- 20 being capable, when present in and/or on the protected modified catalyst support, of suppressing the solubility of the protected modified catalyst support in the aqueous solution.

17. A method according to Claim 16, which includes washing

25 the protected modified catalyst support to remove any residual solvent, with a slurry comprising the washed catalyst support and washing liquid being formed, and drying the slurry.

18. A method according to Claim 17, wherein the washing is

30 effected with an aqueous solution, and is effected at a temperature of about 60°C for about 1 hour.

19. A method according to Claim 17 or Claim 18, wherein the drying of the slurry is effected at a temperature of about 95°C, and under a vacuum of between 0.03 bar(a) and 0.2 bar(a).

5

20. A method of forming a catalyst precursor, which method comprises mixing a protected modified catalyst support obtained by the method of any one of Claims 1 to 19 inclusive, with an aqueous solution of an active catalyst component or its precursor, to form a  
10 slurry, and impregnating the protected modified catalyst support with the active catalyst component or its precursor, to form the catalyst precursor.

21. A method according to Claim 20, wherein the mixing of  
15 the protected modified catalyst support and the active catalyst component or its precursor aqueous solution, and the impregnating thereof, comprises subjecting a slurry of the protected modified catalyst support or carrier, water and the active catalyst component or its precursor to a sub-atmospheric pressure environment, drying the  
20 resultant impregnated carrier under a sub-atmospheric pressure environment, and calcining the dried impregnated carrier and, optionally, repeating the impregnation drying and calcination if a higher active catalyst component loading is required, thereby to obtain the catalyst precursor.

25

22. A method according to Claim 20 or Claim 21, wherein, during the impregnation, a water soluble precursor salt of platinum or palladium is added, as a dopant capable of enhancing the reducibility of the active component, with the mass proportion of dopant to active  
30 catalyst component being between 0.01:100 and 0.3:100.

23. A method of forming a catalyst, which includes reducing or activating a catalyst precursor obtained by the method of any one of Claims 20 to 22.

5 24. A method according to Claim 23, wherein the reduction or activation is effected by subjecting the precursor to heat treatment under the influence of a reducing gas to obtain the catalyst.

25. A process for producing hydrocarbons, which includes  
10 contacting a synthesis gas comprising hydrogen ( $H_2$ ) and carbon monoxide (CO) at an elevated temperature between 180°C and 250°C and an elevated pressure between 10 and 40 bar with a catalyst obtained by the method of Claim 23 or Claim 24 to obtain hydrocarbons, by means of a slurry phase Fischer-Tropsch reaction of  
15 the hydrogen with the carbon monoxide.

26. A novel method of treating an untreated catalyst support, substantially as described and illustrated herein.

20 27. A novel method of forming a catalyst precursor, substantially as described and illustrated herein.

28. A novel method of forming a catalyst, substantially as described and illustrated herein.

25

29. A novel process for producing hydrocarbons, substantially as described and illustrated herein.

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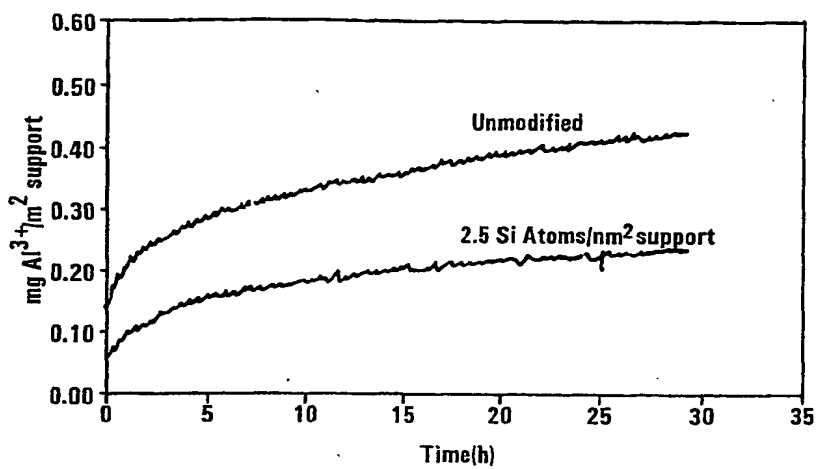


FIG 1

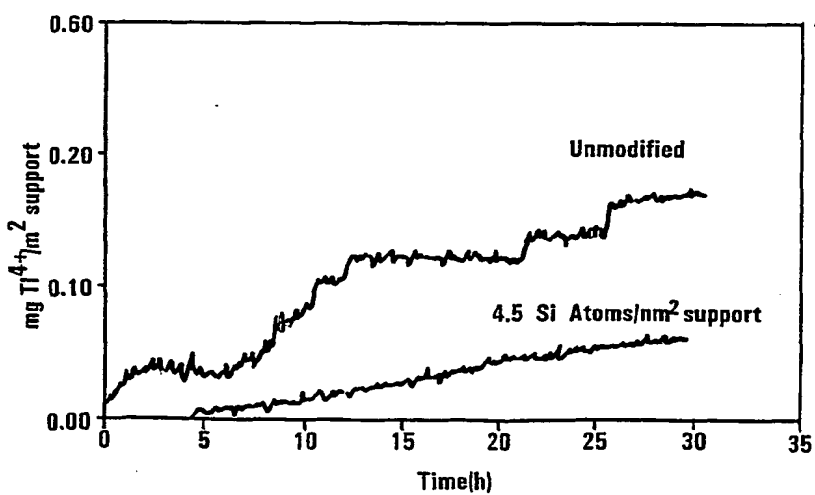


FIG 2

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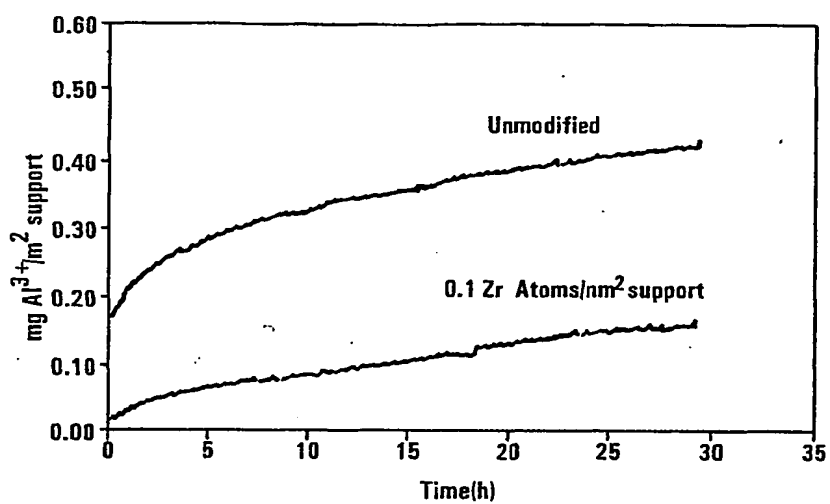


FIG 3

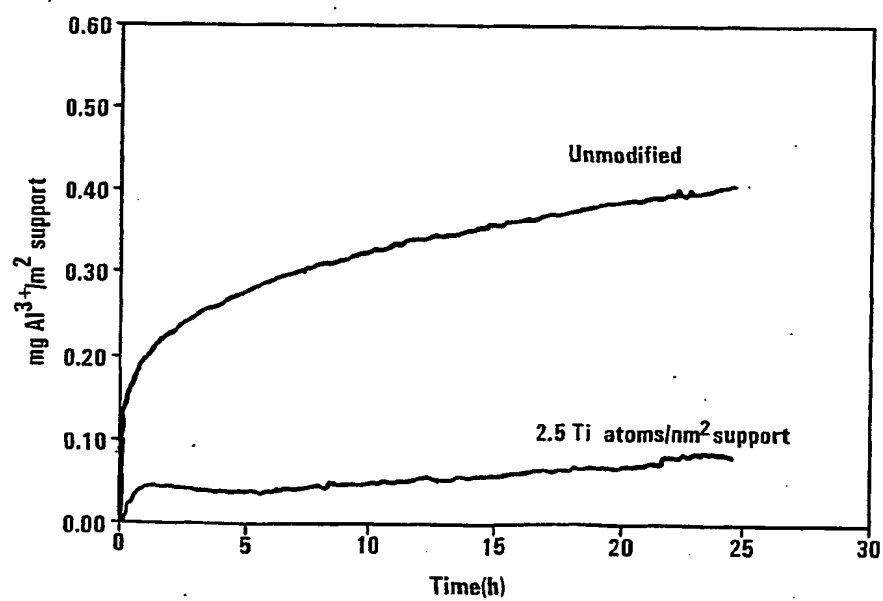


FIG 4

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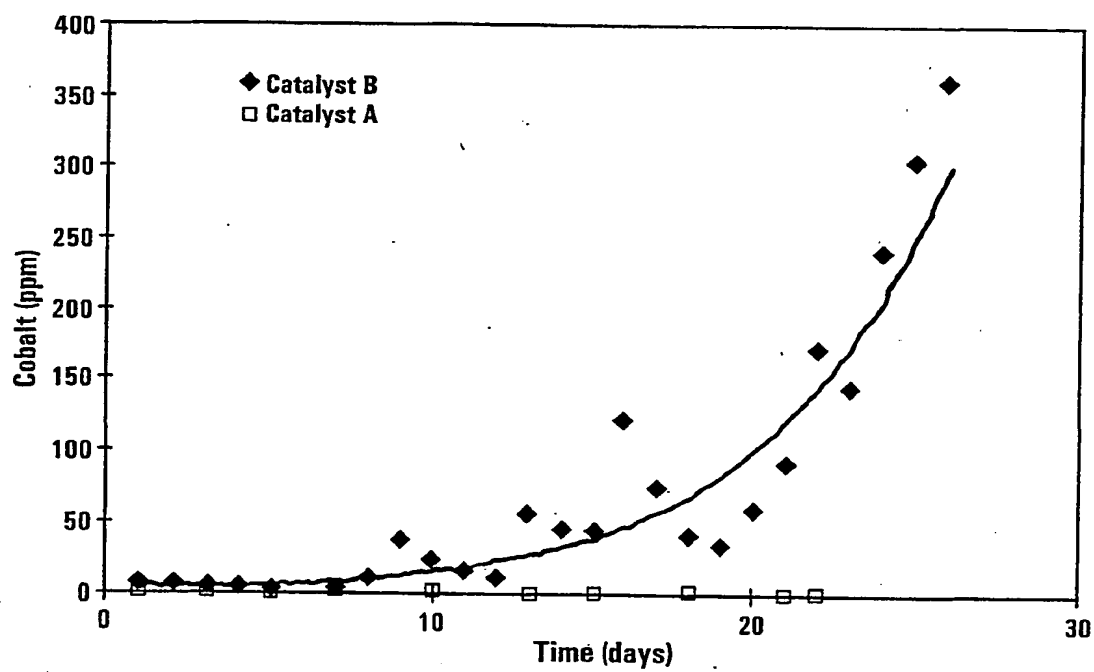


FIG 5